

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US04/024232

International filing date: 28 July 2004 (28.07.2004)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/490,969
Filing date: 29 July 2003 (29.07.2003)

Date of receipt at the International Bureau: 07 April 2005 (07.04.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
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APPLICATION NUMBER: 60/490,969

FILING DATE: *July 29, 2003*

RELATED PCT APPLICATION NUMBER: PCT/US04/24232



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**PROVISIONAL APPLICATION FOR PATENT
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19589 U.S. PRO
60/490969
07/29/03

This is a request for filing a Provisional Application for Patent under 37 CFR 1.53(c)

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Title: **METHOD FOR APPLICATION OF A THERMAL BARRIER COATING AND RESULTANT STRUCTURE THEREOF**

21 Sheets of specification.

Included Sheets of drawings.

University of Virginia Patent Foundation claims small entity status as a nonprofit organization (37 CFR §§1.27(a)(3) and (c)). The Commissioner is hereby authorized to charge the Small Entity Fee of **\$80** to Deposit Account No. 50-0423.

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This invention was made by an agency of the United States Government or under a contract with an agency of the United States Government. The government has certain rights in the invention.

YES ☒ NO ☐ ONR Grant Nos. N001014-98-1-0355; N00014-00-1-0147; and N00014-97-97-0106

Dated: July 29, 2003

Respectfully submitted,

By:


Robert J. Decker (Reg. No. 44,056)

Method for Application of a Thermal Barrier Coating and Resultant Structure thereof

BACKGROUND OF THE INVENTION

Thermal Barrier Coatings are used extensively in aircraft and industrial gas turbine engines. They typically consist of a metallic (or intermetallic) bond coat and a ceramic top coat. The bond coat is used to provide oxidation and hot corrosion protection for the substrate, usually a nickel or cobalt based superalloy, and to produce a thermally grown oxide (TGO) which provides adhesion for the top coat. The top coat is a yttria stabilized zirconia material (typically 7-8 wt. % yttria with the balance zirconia) that provides thermal insulation to the underlying metal. By insulating the metallic component, its temperature is reduced allowing it to last longer or to survive with less cooling air (cooling air reduces the performance of the engine).

SUMMARY OF INVENTION OF THE INVENTION

We claim a process recipe, and resulting structure, for depositing ceramic coatings with preferred coating density, morphology and adherence for applications such as thermal protection of internally cooled components. Such components are found in the hot sections of gas turbine and diesel engines and in turbo machinery. These coatings require a low thermal conductivity in the through thickness of the coating, high in-plane elastic compliance, high erosion and foreign object damage resistance and resistance to hot corrosion. These performance characteristics are determined by the coatings composition, the coatings morphology and the manner in which the coating is applied. Today's coatings applied by either an air plasma spray or electron beam evaporation process that operates under high vacuum. This latter process results in a process recipe that creates a preferred morphology of the coating. The present invention reported here utilizes a high pressure, directed vapor deposition process in which evaporation is achieved by electron beam heating, laser ablation / evaporation, resistance heating or other mechanisms of evaporation. Because the present invention process is different to the conventional EB-physical

vapor deposition process used currently, it results in a different process recipe for creating a preferred coating. It is this new process recipe and resultant structure that we disclose in this invention.

SUMMARY OF THE DRAWINGS

Figure 1 – Micrograph showing a YSZ top coat applied using EB-PVD.

Figure 2 – Plots showing the preferred process conditions for depositing thermal barrier coatings.

Figure 3 – Plot showing the angle of incidence distribution for the cases of DVD and EB-PVD.

Figure 4 -- a) DVD has the ability to combine focused evaporation with plasma activation for rapid, efficient deposition of various crystal structures. b) X-ray scans reveal the effect of plasma activation upon atomic structure.

Figure 5 – Experimental and Direct Simulation Monte Carlo data showing the effect of chamber pressure and pressure ratio on the deposition efficiency of copper deposited onto a 5.08 cm diameter disc located 10 cm from the evaporation source.

Figure 6 – Deposition efficiency of Aluminum deposited onto a 380 micron diameter fiber located 15 cm from the vapor source. A chamber pressure of 16 Pa is used in the EB-DVD cases. The use of a gas jet results in a more focused flux that enables a 10x increase in efficiency over EB-PVD. However, the deposition efficiency is relatively unaffected by increasing the pressure ratio because although increasing the pressure ratio decreases the area of the evaporated flux (i.e. more focused flux) it also decreases the amount of NLOS coating that occurs.

Figure 7 – Schematic illustration of the e-beam orientation in one configuration of a DVD processing system.

Figure 8 – XRD pattern showing the formation of an alpha alumina layer on a nickel aluminide bond coat using a vacuum heat treatment

DETAILED DESCRIPTION OF THE INVENTION

Vapor phase processes are widely used for applying thermal and environmental protection coating systems to components. They are widely used to protect the hot structural components of many gas turbine engines that must operate at temperatures approaching their melting point [1]. As gas inlet temperatures continue to rise, failure by thermally-induced mechanisms has been avoided by making airfoil components with internal cooling conduits, and injecting compressor discharge air to decrease the component temperature [2]. To maximize engine efficiency, however, it is desirable to minimize the use of this air for cooling purposes. Traditionally, this has been accomplished by designing more efficient cooling geometries within the component and by film cooling of the component surface using drilled holes. These approaches have now matured and alternate strategies that exploit the insulating abilities of thermal barrier coatings (TBC's) are being investigated for the thermal protection of engine components.

The TBC systems currently in use are multilayer systems consisting of an yttria partially-stabilized zirconia (YSZ) top layer that thermally protects the superalloy component, and an underlying MCrAlY (M = Ni, Co) or nickel aluminide bond coat which improves the YSZ adhesion. The YSZ layer has a relatively high thermal expansion coefficient to limit thermally induced strains and a low thermal conductivity resulting in surface temperature reductions of up to 170°C [3]. This layer is well bonded to a thin (approximately 1 μm) thermally grown (aluminum) oxide (TGO) layer which impedes oxidation and hot corrosion of the underlying component [4]. This TGO layer is formed on the surface of the aluminum-rich alloy layer (bond coat). Either a low pressure plasma spray [5] (LPPS) or pack cementation [6] approach is used to apply the bond coat layer. The high temperature oxidization environment present prior to and during deposition leads to growth of a thin TGO layer at the interface between the TBC and the bond coat layer [7]. The generated YSZ layer consists of a "nontransformable" tetragonal (t') phase having a complex microstructure consisting of twins and anti-phase boundaries. This microstructure yields a thermomechanically tough coating which has been shown to improve TBC performance by limiting crack propagation in the YSZ layer [8].

To date, the lowest cost TBC's have been applied using the plasma spray (PS) process, such as an air plasma spray (APS) process. The approach employs a plasma or combustion torch

to melt and spray deposit YSZ droplets onto airfoil substrates. These deposits contain disc-like pores in the plane of the coating resulting in a YSZ top layer that has an extremely low thermal conductivity. This is due to the high thermal resistance of the pores oriented normal to the heat flow direction. Unfortunately, these layers also have poor spallation resistance, resulting from a combination of the disc-like coating defects and the large thermal expansion mismatch between the YSZ layer and the bond coat [9]. This lack of reliability limits these coatings to component life extension at current operating temperatures (i.e., they cannot be used to increase engine temperature).

More recently, TBC's have been produced by electron beam-physical vapor deposition (EB-PVD). Using this technique the YSZ layer has a columnar microstructure with elongated inter-columnar voids aligned perpendicular to the substrate surface. This structure results in a low in-plane stiffness that limits thermomechanical stresses on heating/cooling and improved spallation resistance compared to the LPPS layers [10]. The columns exhibit a tapered shape, growing wider with increased thickness, a faceted surface and a strong {200} crystallographic texture [11]. Failure in these coatings no longer occurs within the YSZ layer but at the TGO/bond coat interface. This failure path appears to result from large stresses within the TGO layer, which increase with oxidation induced layer growth in service [12, 13]. For turbine blade applications, EB-PVD TBC's have the further advantages of limiting the undesirable blocking of air cooling holes during deposition and generating a smoother, more aerodynamic surface [14]. However, EB-PVD coatings have a higher thermal conductivity than their LPPS counterparts [15] and are more costly to apply (due to high equipment costs, deposition efficiencies of about 2-5 percent of the evaporated flux, and relatively slow (approximately 5 micrometers (μm) min^{-1}) deposition rates) [16]. To make vapor phase deposited TBC's a viable means for increasing engine performance, improved deposition techniques/strategies are needed.

The cost of the EB-PVD coatings can be as much as ten times that of PS coatings. The higher equipment costs of EB-PVD are a result of the high vacuum environment that is necessary during deposition (e.g., typically below 10^{-6} Torr), high cost of high power electron beam guns, and sophisticated component manipulation needed to achieve acceptable coatings. The operating pressure defines the vacuum pump requirements with lower pressures generally needing more expensive pumps. The low deposition rate and low materials utilization efficiency (MUE) of

EB-PVD is related to the distribution of the vapor flux as it leaves the evaporated source. Generally, the vapor flux spreads out from the source with a distribution described by a $\cos^n\theta$ function (where $n = 2, 3, 4$ or more, and θ is the angle to the normal axis). The general alignment of the normal axis is referred to herein as the main direction. When relatively long source-to-substrate distances are required (e.g., as in YSZ deposition using EB-PVD where this distance often approaches 50 cm to avoid substrate overheating) deposition efficiency is dramatically decreased to 1-5 percent of the evaporated flux and the deposition rate is proportionally reduced. To overcome the low deposition rate, the evaporation rate from the source materials is raised by increasing the electron beam power. However, this is costly and during YSZ evaporation, increased beam power leads to the production of molten droplets of material rather than atomistic vapor. This produces coating defects, and as a result, other approaches must be used to increase deposition rates. The high cost of deposition also impedes the use of physical vapor deposition methods for the deposition of bond coats.

The low deposition efficiency results from flux spreading beyond the periphery of the sample. One approach to reduce the spread of the flux exploits entrainment of the vapor in a controllable inert (e.g. helium or argon) carrier gas flow [17]. Such an approach is used in electron beam directed vapor deposition (EB-DVD). In this approach, the combination of a continuously operating 60 kV/10 kW axial e-beam gun (modified to function in a low vacuum environment) and an inert carrier gas jet is used. In this system the vaporized material is entrained in the carrier gas jet created using a converging / diverging nozzle configuration and deposited onto the substrate or target at high rate and with a high materials utilization efficiency [18]. Preliminary results have shown that YSZ layers having a columnar structure, a low thermal conductivity, the t' phase structure and a (200) texture can be produced using this technique [19]. Therefore the use of EB-DVD to produce low cost TBC's appears feasible.

There exists a need in the art for a cost-effective method to apply high quality TBC top coatings to surfaces. The present invention addresses this need and provides, among other things, how to manipulate the process conditions in a EB-DVD systems to deposit high quality, highly efficient TBC top coats as well as how to deposit high quality TBC top coats onto positions that are that in the line-of-sight of the vapor source.

I. Highly Efficient Top Coats

The thermal protection of the top coats of thermal barrier coating system produced by electron beam – physical vapor deposition (EB-PVD) has a relatively high density (80 to 95% of the bulk value for YSZ), columnar morphology. At the bottom of the coating where deposition first occurs many, randomly orientated grains are formed. Columnar structures evolve with a tapered shape, a (200) texture and a faceted surface. The columns contain porosity. Vapor deposited coatings with this structure are effective top coats that yield a long lifetime, good erosion resistance and adequately low thermal conductivity.

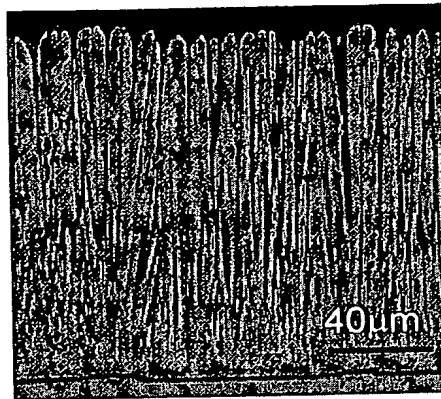


Figure 1 – Micrograph showing a YSZ top coat applied using EB-PVD.

Thermal barrier coatings can also be produced using a directed vapor deposition approach. In this approach the evaporant is entrained in a gas jet and transported to the substrate where it is deposited. This approach can be used to create top coats that are very similar to those produced using EB-PVD (but in a much more economical manner) as well as top coats that are very different from conventional coatings. Both may have utility for engine component protection.

The morphology of DVD deposited top coats is strongly dependent on the process conditions used. If the rate of evaporation is sufficiently low, and the atoms/molecules of the gas high enough velocity to entrain, dilute and transport the vapor to the substrate an atomic/molecular flux is presented to the component for deposition. The angle of incidence this

flux makes with the substrate is broadly distributed. The width of the distribution is controllable by adjusting the flow conditions used to create the gas jet. Changing the process conditions to cause high rate evaporation, low gas jet atom velocity and high vapor concentration in the jet results in gas phase cluster formation and the presentation of mixed atomic / molecular + cluster flux for deposition on the surface of the component. Conditions that limit the vapor phase nucleation and growth of clusters and the divergence of the vapor incidence angle distribution from EB-PVD conditions allow top coats similar to those made by EB-PVD to be deposited. In DVD this can be done with a much higher deposition efficiency that enables a reduced evaporation rate to meet a target deposition rate and results in a more economical utilization of the source material.

Critical process conditions for the deposition of top coats include: substrate temperature, chamber pressure, pressure ratio, evaporation rate, substrate rotation rate. For each parameter a process range can be defined over which conventional coatings can be applied.

- a) Substrate temperature: The maximum temperature is defined by the melting point of the substrate (or its maximum exposure temperature). The minimum temperature is limited by the coating density. This minimum temperature is the same as the EB-PVD process ($\sim 900^{\circ}\text{C}$). As the chamber pressure and evaporation rate increase the minimum allowable temperature will become gradually higher.
- b) Chamber Pressure: The maximum chamber pressure is defined as the pressure at which the vapor phase nucleation and growth of clusters and the divergence in the vapor incident angle distribution deviates significantly from EB-PVD conditions. From DSMC simulations and experimental work this is typically between 0.01 Torr and 1.0 Torr. Higher pressures can be allowed as the substrate temperature is increased. The minimum chamber pressure is defined by the pressure that results in a mean free path that is greater than the source-to-substrate distance. At this chamber pressure the gas jet will not effect the vapor flux. For a source-to-substrate distance of 20 cm this value is 0.0085 Pa.
- c) Pressure Ratio: The minimum pressure ratio must be greater than 1.0 to allow carrier gas flow towards the substrate. This is often higher (> 2.2). Increased

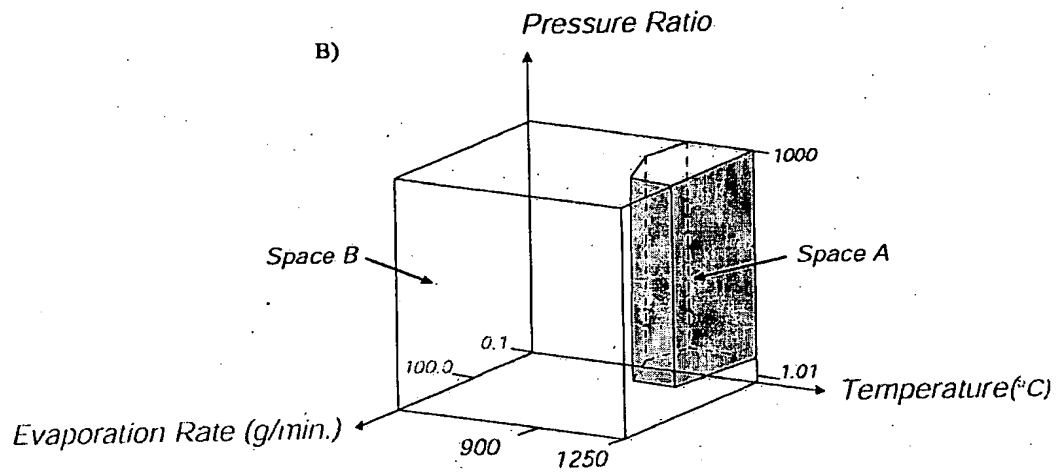
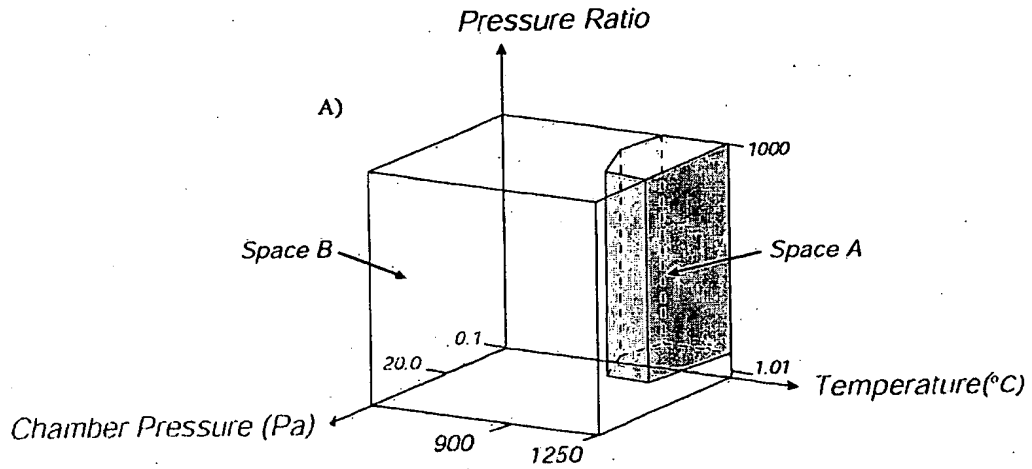
pressure ratios improve the process efficiency and limit the formation of vapor phase clusters. The maximum pressure ratio is controlled by the pumping rate of the chamber pumps and the area of the gas jet nozzle opening.

- d) Evaporation Rate: This should be as high as possible. The maximum is defined by the formation of vapor phase clusters due to the increased the vapor density.
- e) Substrate Rotation Rate: The minimum rotation rate is 1 revolution during the time required to coat a part. No maximum is defined.

The combination of these limitations can be used to define a process space that allows the deposition of coatings having similar structures as EB-PVD. This process space (space A) is most conveniently displayed with a series of three axes plots, **Figure 1**. A table of the process ranges is also given, **Table 1**.

Table 1 -- The process ranges of depositing a TBC top coat with a coating morphology similar to EB-PVD.

Parameter	Minimum	Maximum
Chamber Pressure	0.1 Pa	20 Pa
Pressure Ratio	1.01	1000
Substrate Temperature	900°C	1250°C
Rotation Rate	0	Infinite
Evaporation Rate (0.5" diameter source)	0.1 g/min	100.0 g./min.



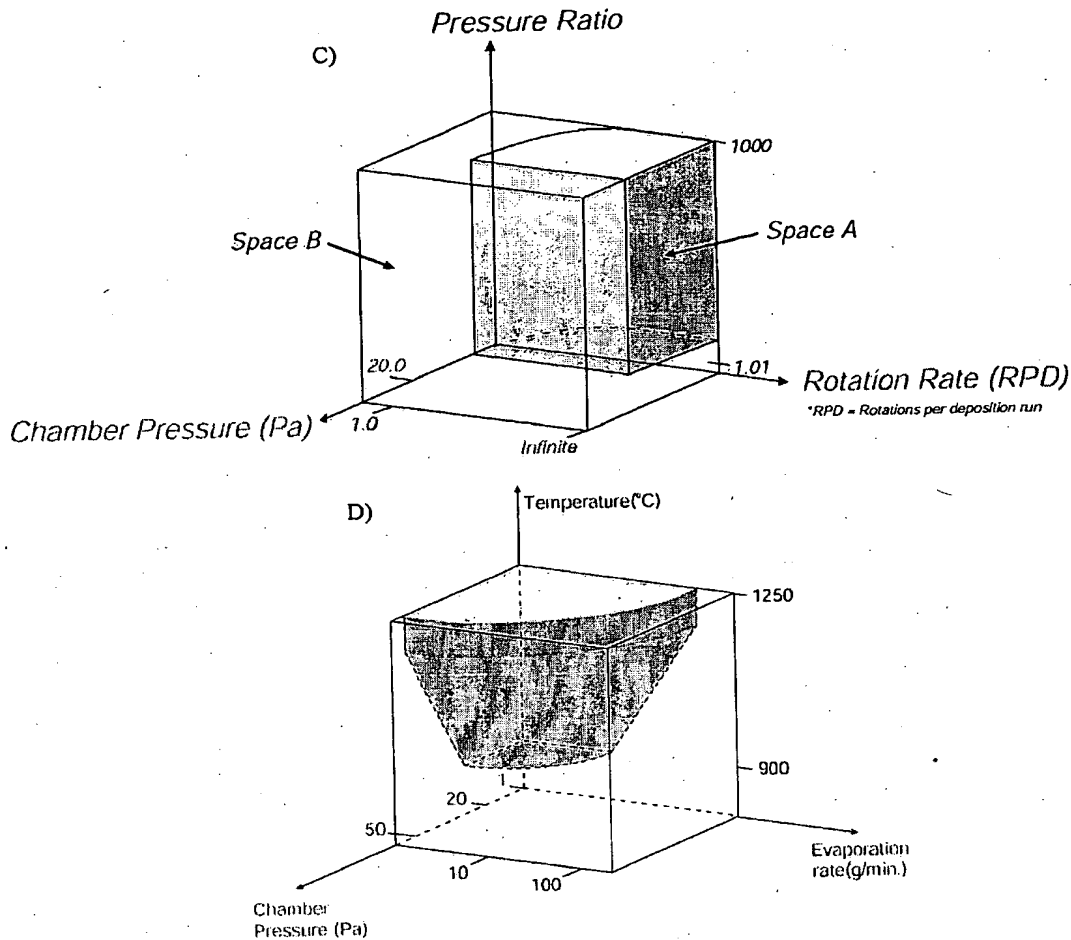


Figure 2 – Three dimension plots (a-c) defining the process space for the deposition of TBC topcoats having a similar morphology to that of EB-PVD deposited top coats.

II. NLOS TBC Top Coat Deposition

The process space for Directed Vapor Deposition is much larger than that defined above as defined in Table 1. The space outside that defined in section 1 (space B) can also be used, however, to create top coats. The morphology of top coats produced in this way are different than that of conventional layers. In these cases, the vapor incidence angle is altered by scattering between and vapor atoms and the gas jet atoms so that it is significantly different to that of in space A, Figure 2. In addition, elevated chamber pressures, low pressure ratios and high evaporation rates will also increase the probability of vapor phase cluster formation. The result

of cluster formation is a change in the coating growth mechanism and typically an increase in the pore volume fraction. This may result in long cyclic oxidation lifetimes, but the increased porosity is expected to limit the erosion resistance of these layers. This process space is also found to be useful for deposited top-coats onto non line-of-sight regions of the substrate.

Table 1 – Available Process Conditions for Directed Vapor Deposition

	Minimum	Maximum
Chamber Pressure	1×10^{-4} Pa	150 Pa
Pressure Ratio	1.01	10000000
Evaporation Rate	0.00001 g/min.	100000 g/min.
Temperature	25°C	1250°C
Rotation Rate	No rotation	Infinite

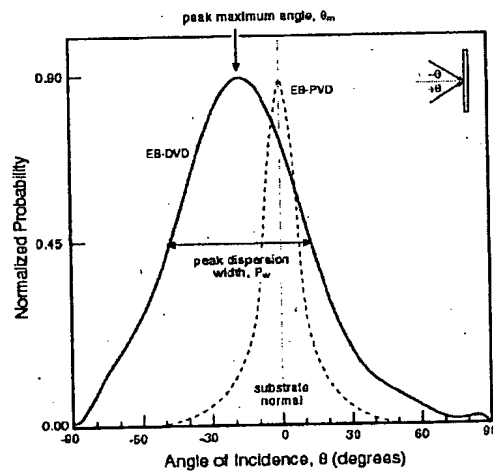


Figure 3 – Plot showing the angle of incidence distribution for the cases of DVD and EB-PVD .

Several approaches can be used to increase the density of coatings deposited in space B:

- A) Increased substrate temperatures during deposition
- B) Use of plasma activation to increase the impact energy of the incident vapor atoms.
- C) Creation of “pressure graded” top coats.

Any temperature increase is limited by the melting point of the substrate. However, plasma activation allows denser coatings even at quite low substrate temperatures. This enables a coating with the standard density to be deposited at higher pressures than without the plasma, Figure 3.

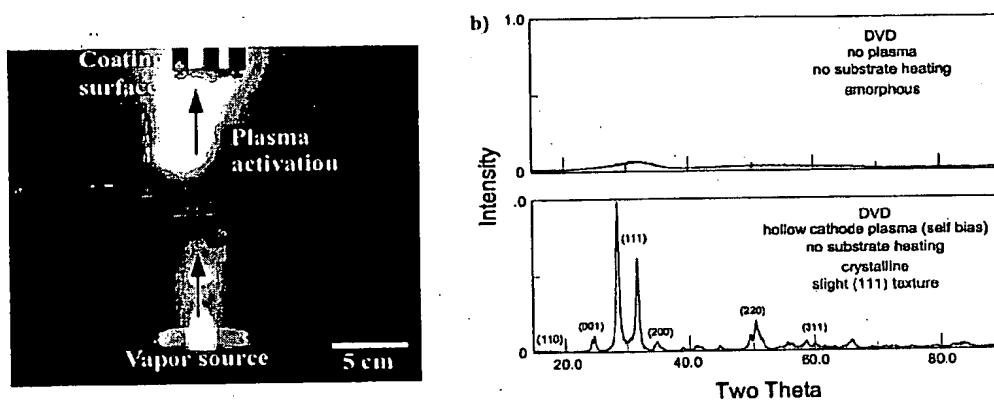


Figure 4 -- a) DVD has the ability to combine focused evaporation with plasma activation for rapid, efficient deposition of various crystal structures. b) X-ray scans reveal the effect of plasma activation upon atomic structure.

The process conditions can also be altered in a controlled manner during the coating run. This enables the coating porosity to be graded through the structure. For example a high porosity may be applied near the substrate and then be steadily increased during the coating run to produce a lower porosity coating (having better erosion resistance) at the coating surface. This can be preformed by systematically increasing the gas flow rate during the run.

Another possibility is the create a multi-layered coating having alternating layers of low and high porosity by increasing and decreasing the gas flow rate (and thus the chamber pressure) during the coating run. Such a coating is expected to have extraordinary thermal protection properties.

III. Deposition Efficiency

As a reference, see co-assigned International Application Nos. PCT/US03/12920, filed April 25, 2003, entitled "Apparatus and Method for Uniform Line of Sight and Non-line of Sight Coating at High Rate and PCT/US03/US02/13639, filed April 30, 2002 entitled "Method and Apparatus for Efficient Application of Substrate Coating," of which all of these patents and applications are hereby incorporated by reference herein in their entirety. When using the process conditions in space A, the deposition efficiency is controlled by the area of the evaporated flux near the substrate with respect to the area of the substrate and the interaction of the gas jet with the substrate. The gas jet substrate interaction should be limited to achieve the highest deposition efficiencies. For a given chamber pressure, the area of the evaporated flux is decreased by increasing the pressure ratio. As the pressure is decreased the pressure ratio must be steadily increased to provide the same "focus" of the flux. However, as the pressure is reduced the interaction between the gas jet and the substrate is also limited. These conditions will result in very high deposition efficiencies, **Figure 4**.

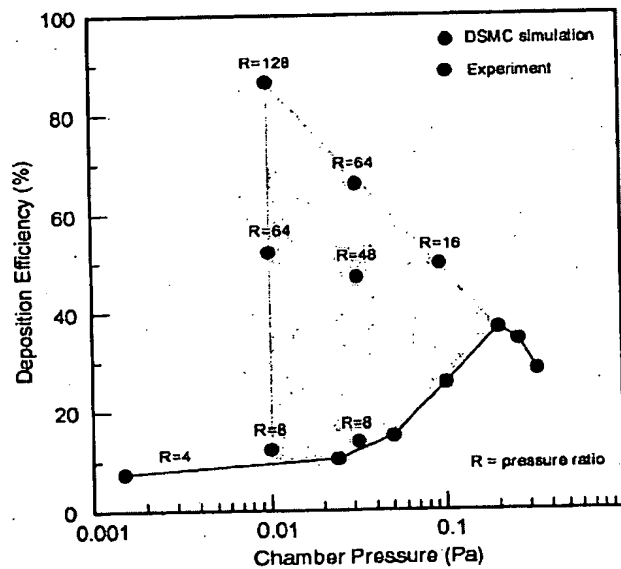


Figure 5 – Experimental and Direct Simulation Monte Carlo data showing the effect of chamber pressure and pressure ratio on the deposition efficiency of copper deposited onto a 5.08 cm diameter disc located 10 cm from the evaporation source.

In space B the situation is more complicated. The deposition efficiency is not only controlled by the area of the evaporated flux near the substrate with respect to the area of the substrate and the interaction of the gas jet with the substrate but also by the degree of non line-of-sight coating that occurs. The highest process efficiency in this case is when high chamber pressures and low pressure ratios are employed. This results in a short mean free path and a moderate gas jet velocity. The result is a moderately focused vapor flux, a limited interaction between the gas jet and the substrate and a high degree of non line-of-sight coating.

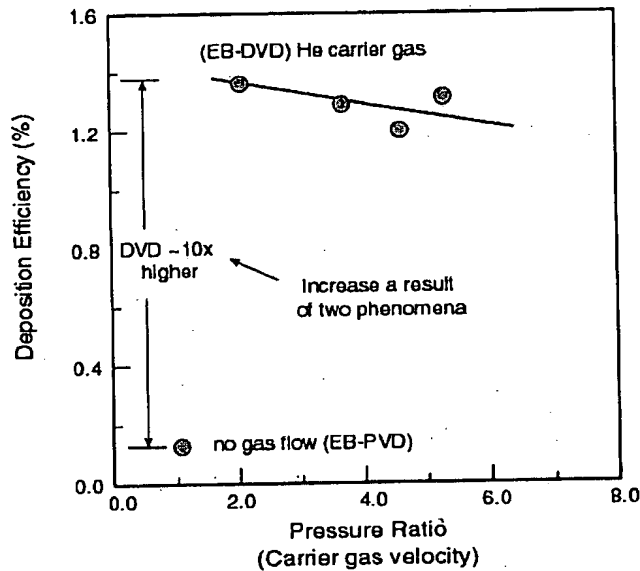


Figure 6 – Deposition efficiency of Aluminum deposited onto a 380 micron diameter fiber located 15 cm from the vapor source. A chamber pressure of 16 Pa is used in the EB-DVD cases. The use of a gas jet results in a more focused flux that enables a 10x increase in efficiency over EB-PVD. However, the deposition efficiency is relatively unaffected by increasing the pressure ratio because although increasing the pressure ratio decreases the area of the evaporated flux (i.e. more focused flux) it also decreases the amount of NLOS coating that occurs.

Plasma activation of the vapor and gas atoms alters their collisional cross section. This in turn alters their mean free path and thus, the degree of non-line-of-sight coating that occurs

during deposition. Increased ionization of the flux will therefore result in NLOS coating in a similar way as increasing the chamber pressure. In addition, the ability to attract the ionized flux to the substrate by applying a bias will also increase the degree of NLOS coating.

IV. Substrate Heating

The component onto which a TBC is applied must be heated during the deposition of conventionally applied top coats using EB-PVD. This is achieved by placing the part in a pre-heating furnace, moving the part into a deposition chamber and then maintaining the part temperature by taking advantage of the radiant heat from the evaporating source. Thus, in the case of EB-PVD the substrate heating is coupled to the YSZ evaporation process.

When using EB-DVD the process is somewhat different. A pre-heater may still be used to initially heat the component, however, the smaller source rod diameter used (in this case 0.5") limits the fraction of electron beam power that is lost to the environment. Thus, additional measures are required to maintain the part temperature or reduce the requirement of high substrate temperatures.

To account for the reduced heat from the source during deposition an additional component heater may also be employed. This may use resistance, radiant or electron beam heating to maintain the proper component temperature. Another approach would be to construct the area around the nozzle and crucible out of zirconia. Then by overscanning the electron beam onto this area during deposition this area could be made to radiate additional heat. These approaches have the advantage of decoupling the evaporation process from the heating process. The addition of a second electron beam gun for component heating is also possible.

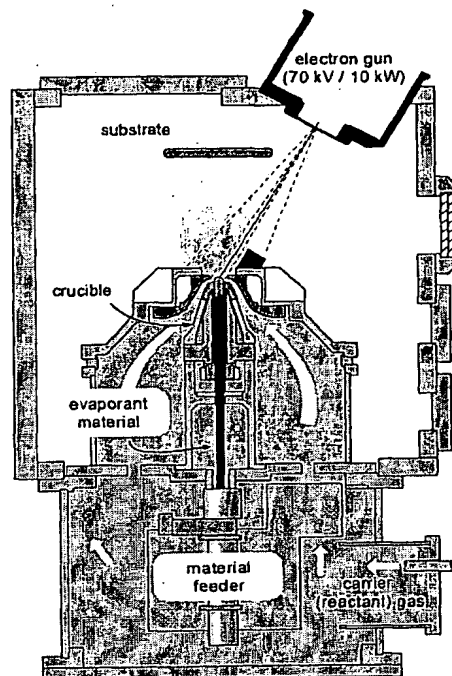
The required component temperatures can also be reduced by using plasma activation to increase the kinetic energy of the depositing atoms.

V. Source Rod

Another important aspect of depositing TBC's using EB-PVD is the ability to uniformly evaporate low thermal conductivity ceramic materials at high rate without any "spitting" from the melt pool or the formation of protrusions from the melt pool that can lead to "spitting". The protrusions can occur quickly when small source sizes are employed, thus a systematic means for

preventing their occurrence is required. An approach used in DVD is to evaporate with an electron beam gun angled 35° from the normal to the source, Figure 5, and rotating the source as it is fed up into the crucible. The rotation requires that any protrusions are pass into the electron beam to a melted before they can grow to an appreciable size.

Figure 7 – Schematic illustration of the e-beam orientation in one configuration of a DVD processing system.



VI. Pre-Treatment of the Substrate

The substrate material that consists of a superalloy and a bondcoat may be heat treated prior to the deposition of the YSZ. This can be preformed in air and in a slight vacuum. An example of an air heat treatment is 1120°C for 1 hour. An example of a vacuum heat treatment is 1120°C for 8 hours at a vacuum pressure of 10^{-4} Pa.

An ionized oxygen flux can also be created using the plasma activation system on the DVD. This can be used to form an alpha alumina layer on the bond coat prior to deposition.

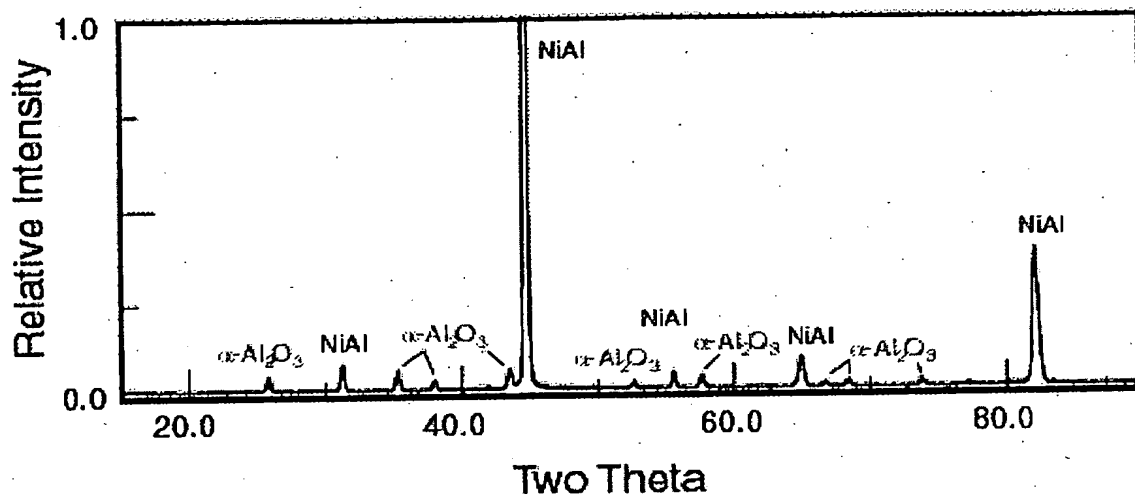


Figure 8 – XRD pattern showing the formation of an alpha alumina layer on a nickel aluminide bond coat using a vacuum heat treatment

VII. Preferred Process Ranges

Highly Efficient TBC Deposition

Based on the above information and that disclosed previously, a preferred process range can be defined for the deposition of thermal barrier coatings using a directed vapor deposition (DVD) process. The process includes a method for evaporating a source rod (any material suitable for a TBC top coat can be used (examples are Yttria Stabilized Zirconia and Gadolinium Zirconate), a method for producing a gas jet, a method for heating the component having the proper pre-treatment and a method for translating and rotating a component. The process ranges

given in Table 2 are desired for depositing a TBC top coat in a highly efficient manner with a coating morphology similar to EB-PVD.

Table 4 -- The preferred process ranges of depositing a TBC top coat in a highly efficient manner with a coating morphology similar to EB-PVD.

Parameter	Minimum	Maximum
Chamber Pressure	1 Pa	20 Pa
Pressure Ratio	11	1000
Substrate Temperature	900°C	1250°C
Rotation Rate	0	Infinite
Evaporation Rate (0.5" diameter source)	0.1 g/min	100.0 g./min.

NLOS TBC Deposition

The preferred process conditions for NLOS coating are given in Hass Conform. They are summarized in Table 3.

Parameter	Minimum	Maximum
Chamber Pressure	5 Pa	50 Pa
Pressure Ratio	1	100
Substrate Temperature	900°C	1250°C
Rotation Rate	0	Infinite
Evaporation Rate (0.5" diameter source)	0.1 g/min	100.0 g./min.

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